(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 941 759 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
15.09.1999 Bulletin 1999/37

(51) Int. Cl.[6]: **B01D 63/06**, B01D 63/02, F28F 21/04, F28F 9/16, C04B 37/00, B28B 23/00 // B01D53/22

(21) Application number: 98200806.2

(22) Date of filing: 12.03.1998

(84) Designated Contracting States:
AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(71) Applicant:
NEDERLANDSE ORGANISATIE VOOR TOEGEPAST-NATUURWETENSCHAPPELIJK ONDERZOEK TNO
2628 VK Delft (NL)

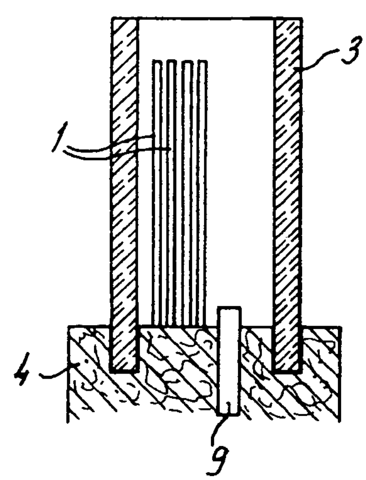
(72) Inventors:
- Brinkman, Hendrik Willem
5673 LV Nuenen (NL)
- Gorter, Harrie
5616 HZ Eindhoven (NL)
- Terpstra, Rinse Alle
5663 JR Geldrop (NL)
- Van der Heijde, Johannes, Coenradus, Thoedorus
5731 MR Mierlo (NL)
- Van Eijk, Joost Petrus Gerardus Maria
NL-5056 BX Berker Enschot (NL)
- Gubbels, Godefridus Hendricus Maria
NL-5704 AX Helmond (NL)

(74) Representative:
de Bruijn, Leendert C.
Nederlandsch Octrooibureau
Scheveningseweg 82
2517 KZ Den Haag (NL)

(54) **Method for producing an exchanger and exchanger**

(57) Method for producing a high temperature resistant exchanger. The exchanger is made from a number of tubes (1) sealingly connected to a pipe plate (12) which is further connected to an enclosure (3). The pipe plate is realised by positioning enclosure (3) and tubes (1) in a mould (4) and pouring a ceramic slurry which is subsequently sintered.

fig-2



EP 0 941 759 A1

Description

[0001] The present invention relates to a method for producing an exchanger according to the preamble of claim 1.

[0002] Such an exchanger can be a heat exchanger, a substance exchanger, or separator. More particular the invention relates to an exchanger to be used at elevated temperature. Because of the conditions of use, ceramic material to provide sufficient service life is used in the art. As example hollow fibre membrane tubes with small tube diameter are mentioned. At higher temperature levels polymer membranes are not longer usable. Advantages of ceramic membranes are high temperature resistivity, mechanical stability and normally those membranes are not sensitive to chemical attack in for example corrosive surroundings. An example for a method to produce a ceramic hollow fibre membrane allowing for high fluxes is disclosed in EP-0 693 961 A1.

[0003] In practical use only tubes are not sufficient. They have to be incorporated in a module to make practical use thereof. Generally such a module comprises an enclosure and a pipe plate for receiving the ends of the hollow tubes as well as possibly further plates to distribute flows both in the hollow tubes and around those tubes.

[0004] Up till now it was technically not feasible to produce in an economical way pipe plates which could withstand relative high temperatures and in which also some mechanical loading is observed and which can be scaled up easily.

[0005] It has been shown that many gas separation processes can be conducted at high temperature with ceramic membranes. An example is the 'Knudsen' separation with gamma-Al_2O_3 membranes, separation of hydrogen from a mixture of gases with silica membranes (300-500°C), isomere separation with zeolite membranes (± 500°C max.) and electrochemical separation of oxygen from air with mixed ionic-electronic conducting materials (800-1000°C). These are only examples for which high temperature exchangers could be used, more in particular the hollow fibre membrane tubes. In order to scale-up these processes high temperature resistant membrane modules allowing for high fluxes have to become available for relative low prices.

[0006] The invention aims to provide a method for producing such a module, a pipe plate respectively for an exchanger to be used at elevated temperature having sufficient strength and manufactured in such a way that it is economically feasible. Of course there should be a perfect sealing between the tubes and the pipe plate.

[0007] This aim is realised with a method as described above having the characterising features of claim 1.

[0008] The tubes to be used according to the invention can be the hollow fibre membranes as described above. However, it should be noted that for other applications hollow ceramic tubes (i.e. having a larger diameter) or metallic tubes can be used. With the casting method according to the invention good sealing properties between the pipe plate and the tubes have been observed whilst even after repeated heating and cooling down of the exchanger no cracks occurred. The method as described in the main claim is economical to realise and provides an exchanger in which the pipe plate is no longer the restricting component for the temperature at which the exchanger can be used.

[0009] The present invention deals with an economically attractive way to join simultaneously a large number of hollow tubes, more specific ceramic hollow fibre membranes, to a substance exchanger, more specific a ceramic membrane module with which liquid separation, gas permeation, gas separation and related processes at high temperature can be conducted. Furthermore, the invention is of importance at high-temperature heat exchanging processes and high-temperature ceramic or inorganic equipment in which leak-free ceramic/ceramic connections are required.

[0010] If the exchanger tubes are hollow fibre membranes, such ceramic membranes are first made as tubes or hollow fibres in shape and condition in which they will be in the completed exchanger. This means that the desired pore size and porosity are already adjusted which can be effected by a heat treatment at elevated temperature, for example as described in EP-0 693 961 (between 1200 and 1650°C)). Ceramic membranes can be porous or (inert) gas tight and can comprise one or more (concentric) layers.

[0011] To obtain a possibility to introduce a fluid around the pipes according to a preferred embodiment of the invention in the pipe plate also a feed/discharge pipe is arranged. To provide sealing it is possible that together with casting the slurry in a mould in or onto which the exchanger tubes are positioned also such a feed/discharge pipe is present. However, it will be understood that such feed/discharge pipes can also be connected to any other part of the enclosure.

[0012] The enclosure according to the invention can comprise a ceramic material and can have any shape known in the art. Preferably it is also placed on or in the mould to provide sealing engagement between the pipe plate and the enclosure.

[0013] In order to realize a plenum for the hollow tubes an end plate has to be provided spaced from the pipe plate. Such an end plate can be produced with the same method as described above for preparing the pipe plate. Dependent from the slurry and its condition used for the pipe plate it is possible that this cast and dried slurry for the pipe plate is still in green condition whilst the end plate is cast so that both the end plate and the pipe plate can be sintered in one step. Of course production in two sintering steps is possible.

[0014] The other end of the exchanger can be produced in the same way and also for this production either separate sintering steps can be used or one general sintering step. In the last case the green strength of the other - opposed - pipe plate will be sufficient to allow

handling of the exchanger to be built. Because the ceramic material resulting from the slurry after sintering has about the same thermal expansion coefficient as other components used in the exchanger (difference less than 5 x $10^{-6}K^{-1}$), thermal tensions in the exchanger are minimized. Also mechanical properties are sufficient either at high temperature and extreme process pressures. For the ceramic material used in the exchanger, use can be made of aluminium oxide, silicon carbide, silicon nitride, zirconium oxide, hydroxyapatite, perovskites and other substances.

[0015] In all these cases, the composition of the ceramic slurry is chosen in such a way that after casting minimum shrinkage occurs during drying and sintering.

[0016] As described above the hollow tubes used can be in finished condition at the moment the pipe plates are cast around them. However, it is also possible to subject the internals of the heat exchangers to a further conditioning before or after sintering. To that end a liquid or vapour can be entered in the related compartment which can provide a coating having the desired properties. It is also possible to introduce two separate liquids or vapours in the two exchanging compartments which will diffuse to each other and react only at their interface in order to obtain the desired properties. In case that the pipe plates and end plates are not gas-tight yet, it may be desirable to apply a gas-tight, leak-free coating on these plates. In this case the ceramic compact gives mechanical strength whereas the coating is responsible for gas-tightness. The components for obtaining coatings or further treating the material of the exchange components can be introduced as sol-gel layer and after filling the related compartments excess material is drained. It is also possible to condition only determined parts of a compartment by appropriate positioning of the related part of the exchanger at introduction of the material to be applied on the related component.

[0017] The invention also relates to a method for producing a high-temperature resistant joint between two or more ceramic articles, wherein said articles are positioned in or onto a mould, the mould is filled with a ceramic slurry, said slurry together with the articles is sintered to a solid ceramic and said solid ceramic is covered with a gas-tight coating. This method can be used both in combination with the method as described above or independently therefrom, i.e. to produce other joint between articles not in the field of exchangers.

[0018] The invention also relates to an exchanger according to claim 11. Surprisingly it has been found that no further sealing is necessary under ordinary conditions to provide a sufficient type fit between the tubes and the pipe plate.

[0019] However, if further sealing is necessary, for example if relatively porous ceramic materials are used, the coating process as described above can be applied.

[0020] The invention will be further elucidated referring to an example shown in the drawings wherein:

Fig. 1 schematically shows some of the components to be used to obtain an exchanger according to the invention;

Fig. 2 - 6 show several steps for the production of the exchanger;

Fig. 7 shows an exchanger according to the invention; and

Fig. 8 shows an additional treatment of the exchanger according to the invention.

[0021] In fig. 1 the hollow tubes on which exchanging/separating is effected are indicated by 1. This can be a ceramic material or metallic material. In a chosen example tubes of ceramic material are used having an external diameter below 2.5 mm and because of that are referred to by hollow fibre membrane tubes. Such tubes are used, for example for separating substances at elevated temperature. However, as indicated above many other applications for the exchanger according to the invention are possible.

[0022] The opening in the tubes 1 is indicated by 2. 3 is an enclosure positioned around the tubes. 4 is a mould to be used to provide a pipe plate. This mould comprises a circular groove 5 arranged to accommodate the free end of enclosure 3. Dead ending openings 6 are provided in mould to receive tubes 1. A relatively larger passage 7 is present in which feed/discharge pipe 9 can be introduced. The mould can be realized from any material known in the art but in this example gypsum is used. Both the enclosure 3 and the feed/discharge pipe 9 are made from a ceramic material.

[0023] To obtain a pipe plate first of all several items are positioned in or onto mould 4 as shown in fig. 2. Subsequently a slurry is casted from above in enclosure 3 to obtain a layer of slurry material having the shape of the pipe plate 12 to be produced. Mould 4 is a relatively porous material being able to absorb the solvent of the slurry so that drying thereof is a relatively simple step. After this slurry is introduced either the mould together with the components as shown in fig. 2 and 3 is sintered or the mould is simply removed. The last step is only possible if the green strength of the slurry material is sufficient to keep several components together.

[0024] Fig. 4 shows the next step in which the pipe plate on the opposite side of exchanger to be built is shown.

[0025] The next step whether or not after sintering is to provide the end plate 14 to delimit the plenum 17 for the tubes. This is shown in fig. 5 wherein the pipe plate produced is indicated with 12 and the further mould used has reference number 16. In this mould except from the feed/discharge pipe 9 also a feed/discharge pipe 15 made from a ceramic material is arranged in order to connect the tubes with the surroundings. Slurry material can be introduced through such pipe 15 up to the top level thereof. After that and making the opposite plate 14 (fig.6) sintering is effected and the heat exchanger generally referred to by 10 as shown in fig. 7

is obtained. Sintering can be effected by heating during about 2 hours at about 1200°C. However, it should be noted that depending from the materials used other sintering conditions which will be obvious for the persons skilled in the art are applicable.

[0026] In a next step coatings can be introduced by flowing a fluid through the exchanger which fluid will be deposited on the related surfaces of the components of the exchanger and provide a more or less gas tight surface. It is possible to apply such coatings on the pipe plates or end plates after producing these plates one at the time.

[0027] An example of a further treatment is shown in fig. 8. Through pipe 9 a sol-gel material is introduced. After filling exchanger compartment 18 above plenum 17 pressure is removed from pipe 9 and excess slurry is allowed to drain back.

[0028] If immediately after manufacturing or after prolonged use leaks appear it is possible to repair such leaks through vapour face deposition or infiltration technique (CVD or CVI) through reactants approaching each other from opposite sides of the leak. These reagents in gas or vapour conditions are introduced through the related feed/discharge pipe. Furthermore it is possible to repair remaining leaks by wet chemical deposition technique through reagents approaching each other from opposite sides of the leaks.

Example.

[0029] Below follows a description for producing a ceramic membrane module for a membrane system comprising an extruded alpha-Al_2O_3 support having a gamma-Al_2O_3 top layer.

[0030] Through the extrusion technique and the subsequent heat treatment at 1250°C a number of alpha-Al_2O_3 hollow fibre membranes have been prepared having an outer diameter of 2 mm, a length of about 20 cm and an average porous size of 0,2 μm and a porosity of about 40%. Before use within the exchange according to the invention the tubes have been cut to a length of 117 mm. As enclosure 3 a commercial obtainable sealed Al_2O_3 tube is used (Alsint, having less than 0,3 vol% open space sold by Ceratec, The Netherlands) having a length of 200 mm, inner diameter of 40 mm and an outer diameter of 50 mm. Four feed discharge pipes 9 are made from the same material having a length of 100 mm and an inner diameter of 4 mm and an outer diameter of 6 mm.

[0031] The gypsum block 4 is machined through drilling and grinding so that the enclosure 3, a feed pipe 9 and twenty hollow fibre membranes 1 can be vertical positioned thereon. The enclosure 3 extends 2,0 cm in mould 4 and the hollow fibre membranes 1 several millimetres. The feed/discharge pipe 9 completely penetrates the gypsum block. Both the feed/discharge pipe and the membranes are positioned inside the enclosure. The tubes all have the same height at their extremity. A ceramic slurry is prepared having the following composition:

1260.2 grams	Al_2O_3 (T60 of Alcoa),
988.2 grams	Al_2O_3 slurry (85 wt% A17NE-slurry of Alcoa),
84.1 grams	demiwater and
1.0 grams	Dolapix CE 64.

[0032] The ceramic slurry contains 90% by weight Al_2O_3.

[0033] About 35 ceramic slurry has been cast in the enclosure around the ceramic tubes 1 and the feed/discharge pipe 9. After drying time of about 1 hour the combination slurry/enclosure/membranes/feed discharge pipe is removed from the gypsum block and has been further dried overnight. The next day this combination is subjected to a heat treatment in air at the temperature of 1200°C during 2 hours having a heating and cooling rate of 240°C/hr, further called 'standardized heat treatment'. Due to the high solid content (90% by weight Al_2O_3) of the slurry, hardly any shrinkage was observed during drying and sintering. Above the slurry cast ceramic compact, i.e. 'connection' a coating is provided based on aluminium oxide. This coating is prepared by mixing aluminium oxide based frit powder type PE-FG-01 (obtainable at PRINTLAS EUROPE) with water and to brush the resultant product on the 'connection'. The coating is cured through the 'standardized heat treatment'. The sealing properties of the connection as such (i.e. slurry cast ceramic compact and its coating) has been tested. Air leaking values in the order of 10^{-10} mol/m^2.s.Pa (tested between 0 and 1 bar) have been measured. Except from the commercial aluminium oxide based frit powder some tests have been conducted with a glass mixture (70 wt% SiO_2 10% Na_2O, 9% CaO, 6% Al_2O_3), mixed with water and also brushed and subjected to a 'standardized heat treatment'. Also the sealing properties of this connection as such is around 10^{-10} mol/m^2.s.Pa. As comparative value silica based H_2 separation membranes have a permeation of around 10^{-7} mol/m^2.s.Pa (see for example A.J.Burggraaf, L.Cot, "Fundamentals of inorganic membrane science and technology", Elsevier, Amsterdam (1966), Chapter 9).

[0034] In a subsequent step above 'combination' is reversed on a gypsum block in which the second feed/discharge tube 9 is positioned. The ceramic membranes all exactly are on the upper face of the mould 4. The enclosure exactly slides around the upper face of mould 4. Again 35 grams ceramic slurry with the composition as mentioned above is casted through the discharge pipe 9 which has already been connected to the first pipe plate. After one hour drying the second pipe plate is removed from the mould, dried overnight and subjected to the standardized heat treatment. Also this second connection is coated with a coating based on frit powder PE-FG-01 and subjected to the 'standardized heat treatment'.

[0035] The third connection, i.e. realisation of the end plate is effected by placing the articled produced up till now on a flat mould 16 through which a further feed discharge 10 extends. 35 gr ceramic slurry having the above composition is fed from below to above and flows around the related feed/discharge pipe inside the enclosure. After drying, removing from the mould and standardized heat treatment also this end plate is sealed with the coating as described above. The second end plate is realized in the same way.

[0036] Now a membrane module based on alpha-Al_2O_3 hollow fibre membranes having an outer diameter of about 2 mm an average pore diameter of 0,2 μm and a porosity of 40% is finished.

[0037] Provision of a gamma-Al_2O_3 top layer at the exterior of the hollow alpha-Al_2O_3 tube membranes is effected by preparing a boehmite sol as described by H.W.Brinkman, 'Ceramic membranes by (electro)chemical vapour deposition', thesis University of Twente (1994), page 25. The exchanger is vertical positioned and the lower feed/discharge pipes 9 are closed. Through upper feed/discharge pipe 9 the boehmite-sol is cast until compartment 18 is completely filled with sol. After about 30 seconds the lower feed/discharge pipes are opened so that the excess sol can flow away. The remaining sol applied to the hollow fibre membranes is dried overnight in the air and converted to gamma-Al_2O_3 top layer through a heat treatment in air at 450°C during 3 hours having a heating and cooling rate of 1.5°C per minute. The exchanger is now ready for use.

[0038] Although the invention has been described above referring to a preferred example it should be understood that many changes can be made which are obvious for the person skilled in the art after reading the above description and within the scope of protection of the appended claims.

Claims

1. Method for producing an exchanger (10) comprising a number of hollow exchanger tubes (1) positioned in an enclosure (3), said tubes being sealingly received at opposed ends in a pipe plate (12), being sealed relative to said enclosure, characterised in that, one of the ends of said tubes is positioned in or onto a mould (4), the mould is filled with a ceramic slurry (8), said slurry together with the tubes is sintered to a solid ceramic, the slurry being chosen such that the thermal expansion coefficient of the solid ceramic pipe plate differs less than $5 \times 10^{-6} K^{-1}$ of the thermal expansion coefficient of said tubes.

2. Method according to claim 1, wherein a feed/discharge pipe (9) connected to the internals of said enclosure is arranged in said mould before introducing said slurry.

3. Method according to one of the preceding claims, wherein said enclosure is placed in, onto, or is part of said mould.

4. Method according to one of the preceding claims, wherein a further spaced plate (14) is produced after the slurry for the pipe plate has been introduced in said mould and is at least self supporting, wherein the tubes and the pipe plate are introduced in or onto a further mould having at least two openings, in which two feed/discharge pipes are placed, which mould is filled with a ceramic slurry, said slurry together with the other parts of the exchanger is sintered to a solid ceramic, the slurry being chosen such that the thermal expansion coefficient of the solid ceramic pipe plate differs less than $5 \times 10^{-6} K^{-1}$ of the thermal expansion coefficient of said tubes.

5. Method according to one of the preceding claims, wherein the hollow exchanger tubes are made of porous aluminium oxide, the enclosure and the feed/discharge pipes are made of dense aluminium oxide, the ceramic slurry comprises more than 85% by weight aluminium oxide, and sintering is effected at about 1200°C during about 2 hours.

6. Method according to one of the preceding claims, wherein after sintering the exchanger is filled with a liquid or vapour cooperating with either one of said tubes, enclosure, pipe plate or further pipe plate to produce a coating.

7. Method according to claim 6, wherein on both sides of the item to be coated or infiltrated a component of the liquid or vapour is applied, said two components and possibly said item itself reacting to form said coating or infiltration.

8. Method according to one of the preceding claims, wherein said slurry comprises a solvent and said mould has solvent absorbing properties.

9. Method for producing a high-temperature resistant joint between two or more ceramic articles, wherein said articles are positioned in or onto a mould, the mould is filled with a ceramic slurry, said slurry together with the articles is sintered to a solid ceramic and said solid ceramic is covered with a gas-tight coating.

10. Method according to claim 9 wherein the ceramic items are made of porous or dense aluminium oxide, the ceramic slurry comprises more than 85% by weight aluminium oxide, sintering is effected at about 1200°C during about 2 hours, the coating is an aluminium oxide based frit which is sintered at about 1200°C during about 2 hours.

11. Exchanger (10) comprising a number of exchanger tubes (1), an enclosure (3) and at both opposed ends of the tubes a pipe plate (12) and at both ends of the enclosure a plate (14) being connected to said enclosure, characterised in that, said plate comprises a ceramic material in direct sealing engagement with the tubes..

12. Exchanger according to claim 11, comprising a heat exchanger.

13. Exchanger according to claim 11 or 12, comprising a substance exchanger.

14. Exchanger according to one of the claims 11-13, comprising a ceramic material.

15. Exchanger according to one of the claims 11-14, comprising hollow fibre tubes.

16. Exchanger according to claim 14 or 15, being provided with a coating.

17. Exchanger according to one of the claims 11-16, wherein said enclosure comprises a ceramic tube..

fig-1

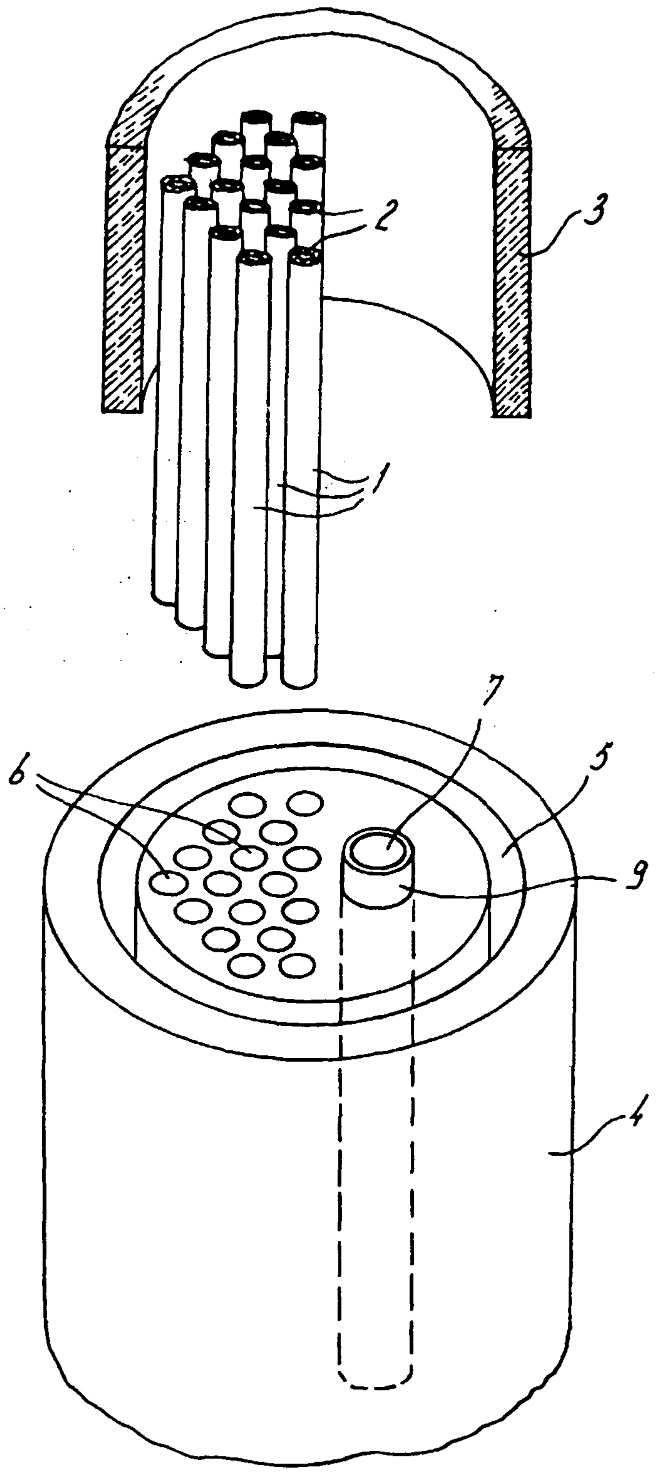


fig-2 fig-3 fig-4

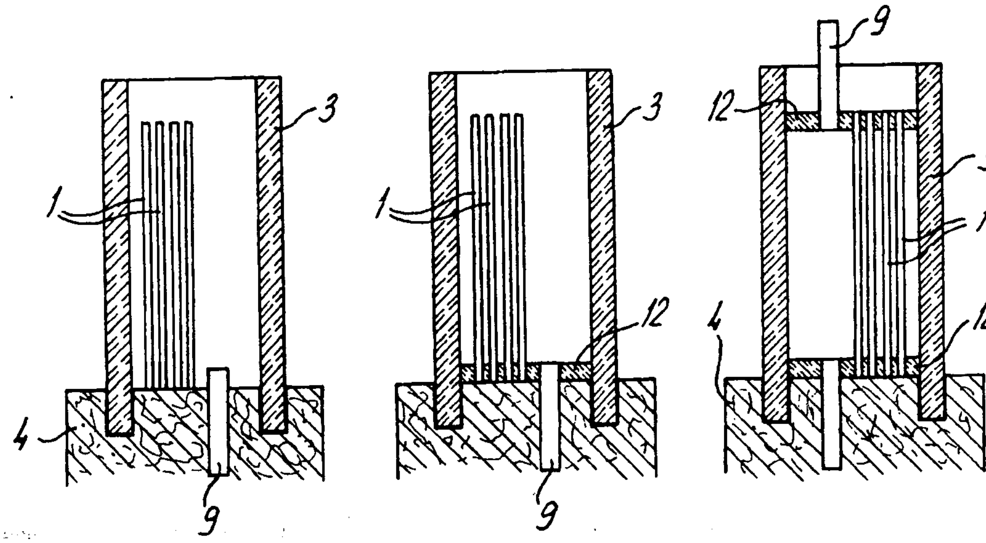
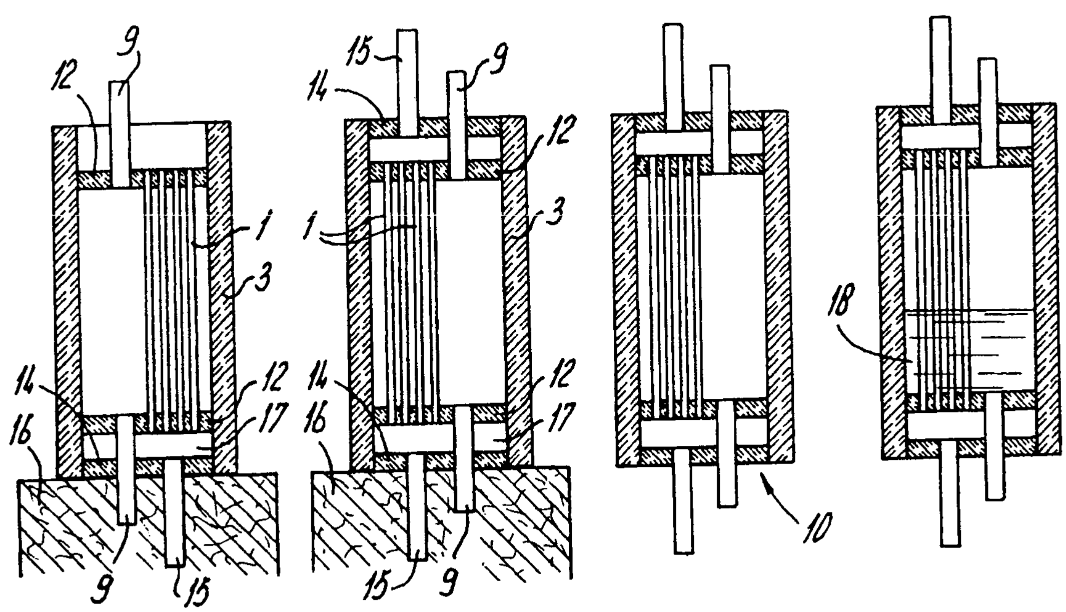


fig-5 fig-6 fig-7 fig-8



European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 20 0806

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	PATENT ABSTRACTS OF JAPAN vol. 010, no. 144 (C-349), 27 May 1986 -& JP 61 004509 A (KOGYO GIJUTSUIN;OTHERS: 0J), 10 January 1986	1,2,11, 13-15	B01D63/06 B01D63/02 F28F21/04 F28F9/16 C04B37/00 B28B23/00 //B01D53/22
Y	* abstract * -& DATABASE WPI Section Ch, Week 8608 Derwent Publications Ltd., London, GB; Class J01, AN 86-051754 XP002074701 * abstract * -& CHEMICAL ABSTRACTS, vol. 104, no. 18, 5 May 1986 Columbus, Ohio, US; abstract no. 151378, XP002074699 * abstract * ---	3,6,16	
A	US 4 296 052 A (ANAND JOGINDER N ET AL) 20 October 1981 * abstract; claims 1-3; figure 1 * * column 2, line 9 - column 4, line 15 * * column 5, line 13 - line 20 * * column 5, line 66 - column 6, line 2 * ---	1,6,11, 13-17	TECHNICAL FIELDS SEARCHED (Int.Cl.6) B01D F28F C04B B28B
X	PATENT ABSTRACTS OF JAPAN vol. 007, no. 007 (C-144), 12 January 1983 -& JP 57 166344 A (TOYO BOSEKI KK), 13 October 1982	11,13-15	
A	* abstract * -& CHEMICAL ABSTRACTS, vol. 98, no. 16, 18 April 1983 Columbus, Ohio, US; abstract no. 131161, XP002074700 * abstract * ---	1,2	

-/--

~~The present search report has been drawn up for all claims~~

Place of search	Date of completion of the search	Examiner
THE HAGUE	17 August 1998	HOORNAERT, P

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 98 20 0806

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP 0 794 403 A (SOLAR TURBINES INC) 10 September 1997 * abstract; claims 1,19-21; figure 2 * * column 1, line 25 - line 28 * * column 3, line 21 - column 4, line 16 * * column 5, line 6 - column 6, line 56 *	11,12, 14,17	
A		1	
X	EP 0 093 612 A (CORNING LTD) 9 November 1983 * abstract; claims 1,3,4,6,7; figures * * page 2, line 5 - page 3, line 30 *	11,12, 14,17	
A		1	
Y	EP 0 165 478 A (GAMBRO DIALYSATOREN) 27 December 1985 * abstract; claim 1; figures * * page 4, line 26 - line 35 *	3	
Y	PATENT ABSTRACTS OF JAPAN vol. 95, no. 8, 29 September 1995 & JP 07 112111 A (NGK INSULATORS INC), 2 May 1995 * abstract * -& DATABASE WPI Section Ch, Week 9526 Derwent Publications Ltd., London, GB; Class E36, AN 95-196389 XP002074702 * abstract *	6,16	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
A	EP 0 092 839 A (CERAVER) 2 November 1983 * abstract; claims 1,8,10; figures * * page 2, line 31 - line 36 * * page 4, line 28 - line 31 *	1,11,13, 14,17	

~~The present search report has been drawn up for all claims~~

Place of search	Date of completion of the search	Examiner
THE HAGUE	17 August 1998	HOORNAERT, P

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

European Patent Office

LACK OF UNITY OF INVENTION SHEET B

Application Number

EP 98 20 0806

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. Claims: 1-8,11-17

   Method for producing an exchanger comprising a number of hollow exchanger tubes positioned in an enclosure, wherein an end of the tubes is placed in a mould, the mould is filled with a ceramic slurry and sintered, the thermal expansion coefficient of the solid ceramic pipe plate after sintering is close to the expansion coefficient of the tubes. Exchanger comprising a number of exchanger tubes in an enclosure and the ends of the tubes being in direct sealing contact with a ceramic pipe plate.

2. Claims: 9,10

   Method for producing a temperature resistent joint between two or more ceramic articles, wherein the articles are placed in a mould, the mould is filled with a ceramic slurry and sintered, and the solid ceramic thus obtained is covered with a gas-tight coating.